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(71) Applicant *(for all designated States except US)*: KEMISK SEPARERING TUMBA AKTIEBOLAG [SE/SE]; S-147 80 Tumba (SE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: STRÖM, Gunnar [SE/SE]; Nöthårsvägen 8, S-757 57 Uppsala (SE). MÅLARSTIG, Björn [SE/SE]; Rallarvägen 7, S-740 20 Brunna (SE).

(74) Agent: CLIVEMO, Ingemar; Alfa-Laval AB, S-147 80 Tumba (SE).

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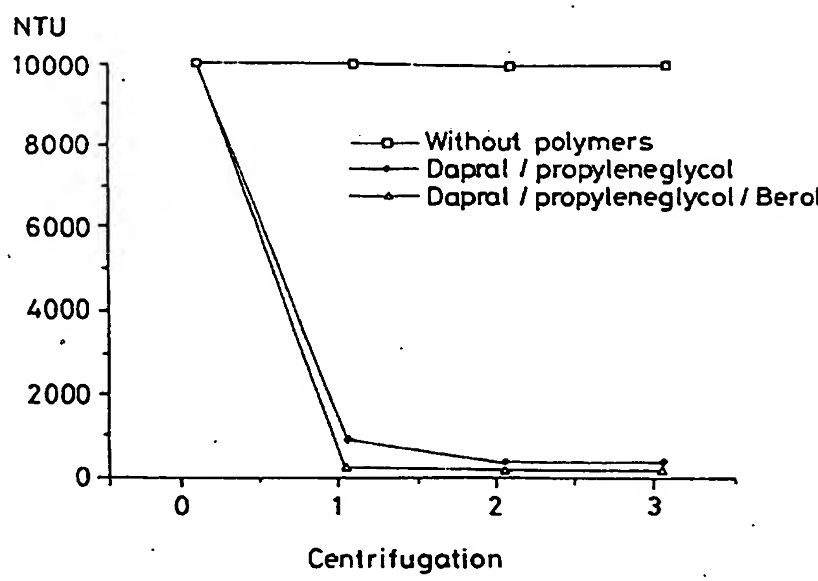
(54) Title: PURIFICATION OF OIL



(57) Abstract

The present invention relates to a method for purification of oil which is contaminated with particles of random density and/or water. A collection polymer or polymer mixture which is insoluble in oil and liquid at room temperature and which has a density which is higher than the oil is added to and mixed with the contaminated oil. The collection polymer and the oil are separated by gravity with or without centrifugation such that the oil forms a top phase and the collection polymer or polymer mixture and the main part of the contaminants form a bottom phase. The bottom phase with the collection polymer and the contaminants is removed.

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Purification of Oil

The present invention relates to purification of oil, which is contaminated by particles of random density and/or water.

Pure oils are commonly used within the industry i.a. for metal working, as lubricating oils and hydraulic oils. The total consumption was estimated to be about 10 000 tons for metal working liquids, 55 000 tons for lubricating oils and 35 000 tons for hydraulic oils in Sweden 1986. Straight (pure) oils 1980 represented 7 000 tons, emulsions 3 000 tons (concentrate) and synthetics 1 000 tons (concentrate) of the metal working liquids.

Metal working liquids are used as cooling and lubricating agents at cutting working such as turning, milling, drilling, grinding and so on and in different types of plastic machining as milling, pressing and drawing.

The use of metal working liquids is the largest within iron, steel and engineering industry. The main tasks for the metal working liquids are to reduce the friction between tool and work piece by lubrication, and to remove the heat which has been formed, i.e. to cool. In the case where the lubricating ability is the most important a straight oil is chosen, while for example at higher working rates where the cooling ability is important, an oil emulsion or a synthetic one is often chosen.

The main components in the straight cutting oil are refined mineral oil and vegetable or animal oil. If necessary the fatty oils have been replaced with

synthetic derivatives of the same for example methyl esters of tallow fatty acids and isopropyl oleate. In order to obtain a well working lubricating film certain EP-additives (Extreme Pressure) are also added which among all may consist of sulphur, chlorine or phosphorous compounds.

However, the properties of the oils get worse with the usage time due to contamination. Particulate contaminants in the oils are often of the type metal particles, rust, oxidation products (coke particles) from the oil. Other not desirable contaminants are water, cellulose fibres, carbon, dust and other organic particles.

In the prior art there are mainly known the following three types of purification of oil:

* Mechanical filtration - the oil is brought to pass through relatively thin (about 0.25-2 mm) "paper" or through thick layers where the oil has a long way to pass. The filters consist of different fibre materials.

* Electrostatic purification - the oil is pumped through an electrostatic field (10 kV) where statically charged particles will move across the flow direction of the oil. The particles then get caught on collectors of pleated paper material.

* Centrifugation type centrifugal separators - in a centrifuge liquid and particles are separated, as soon as the densities are different. This makes it possible to separate particles which are lighter or heavier than the liquid.

The known methods have different advantages and disadvantages. For separation of emulsified water from oil centrifugal separator are to be preferred. Hitherto there is no satisfactory solution for separation of all kinds of particulate contaminants and water from oil.

The present invention solves the problems mentioned above by a method for purification of oil which is contaminated by particles of random density and/or water. The method is mainly characterized in that a collection polymer or polymer mixture which is insoluble in oil and which is liquid at room temperature and has a density which is higher than the oil is added to and mixed with the contaminated oil. The collection polymer and the oil are separated by gravity with or without centrifugation such that the oil forms a top phase and the collection polymer or polymer mixture and the main part of the contaminants form a bottom phase. The bottom phase with the collection polymer or polymer mixture is removed.

The word "particles" refers to all kinds of substances, cells and cell remains.

The oils to be purified may consist for example of lubricating oils, hydraulic oils, rolling oils or quench oils.

The collection polymer or polymer mixture consists of polymers with a relatively low molecular weight.

The used polymer or polymer mixture may consist of different alkylene glycols or polyalkylene glycols based on ethylene or propylene and different copolymers of ethylene oxide (EO) and propylene oxide (PO).

The choice of collection polymers depend on the actual contaminants. If the contaminating particles have a surface structure of a hydrophilic nature then a polyethylene glycol with a rather low molecular weight may be chosen (100-300). If the surface structure of the particles is mainly of hydrophobic nature then a blockpolymer of ethylene oxide (EO) or propylene oxide (PO) with a high content of PO may be used (Molecular weight 4000-8000).

The used amounts of collection polymers may be up to 1 %, preferably only 1-5 ‰ of the amount of oil.

The invention will be described further with reference to the trials and drawings described below, in which

Fig. 1 shows a step-by-step purification of a cutting oil with and without addition of polymers; and

Fig. 2 is a phase diagram for polypropylene glycol 425 and phosphate buffer.

Fig. 3 Arrangement for purification of oil and regeneration of collection polymers.

<u>Trial 1 Separation of polymer particles from mineral oil with different polymers</u>

To a basic oil, PA 06 (Nynäs Petrolium) polymer particles with a median diameter of 4.3 µm (Expancel 051 DC) are added. The concentration of particles was measured by means of a HACH turbidimeter (Svenska Merkanto AB, Uppsala, Sweden). 8 g particle contaminated oil and 0.2 g of the polymers and polymer mixtures described in Table 1 were added to test tubes of glass containing 10

ml. Polymer/hydroxyethyl-tallow-oil-imidazoline (Berol 594) (Berol Kemi, Stenungsund, Sweden) will in the following be abbreviated as Berol 594.

A test tube containing 8 g particle-contaminated oil without added polymer and a test tube where the collection polymer was replaced by 0.2 g H_2O were used as reference.

The test tubes were mixed thoroughly and centrifuged at 2 000 rpm during 2 minutes, after which 4 ml of the upper oil phase is transferred to clean trays of glass for measurement of the turbidity. The trials were carried out at room temperature.

TABLE 1

Polymer	EO/PO	Viscosity (CSt)	Particle reduction (%)
Propylene glycol (MB Sveda Kemi)	-	62	70
Propylene glycol + Berol 594 (5:1)	-	62	96
Polypropylene glycol 425 (MB Sveda Kemi)	-	80	95
Polypropylene glycol 425 + Berol 594	-	80	97
Breox 50A140 (BP, Chemicals)	1:1	130	51
Breox 50A140 + Berol 594	1:1	130	59
Breox 50A1000 + (BP Chemicals)	1:1	1000	66
Breox 380EP + Berol 594	1:1	1000	74
Breox 380EP + (BP, Chemicals)	1:1	1250-3000	50
Breox 380EP + Berol 594	1:1	1250-3000	45
None			21
Water			44

Addition of small amounts of non-ionic or charged polymers/tensides consisting of ethylene oxide and/or propylene oxide monomers (0.1-10%) to a straight mineral oil containing particulate contaminants results in a turbid solution which after centrifugation alternatively after static separation divides into an oil phase (top phase) and a polymer phase (bottom phase). The particles are after the separation mainly found in the polymer containing bottom phase.

As may be seen from Table 1 centrifugation only of the particle contaminated oil results in a reduction of particles of 21 %. The corresponding result when adding propylene glycol and polypropylene glycol was 70 and 95 %, respectively. When the two non-ionic polymers consisting of both ethylene oxide and propylene oxide (Breox 50A 140 and 50A 1000) were used the reduction of particle was 51 and 66 %, respectively, and for the negatively charged (acrylic acid-grafted) polymer Breox 380EP a separation efficiency of 50 % was obtained.

The mechanism for distribution of the particles in the uncharged systems is probably based on hydrophilic/ hydrophobic interactions between the collection polymers and the surface structure of the particles. An addition of the positively charged polymer hydroxyethyl-tallow oil-imidazoline to the polymers resulted except from Breox 380EP in an increased separation efficiency. The best results were obtained after an addition of a positively charged polymer to propylene glycol where an increase from 70 to 96 % was obtained. The corresponding increase for polypropylene glycol was 95 to 97 %. The improved separation depends

most likely on charge interactions between the positively charged hydroxyethyl-tallow oil-imidazoline and negative charges on the surfaces of the particles which may result in formation of micells and thereby an increased solubility of the particles in the polymer phase.

Trial 2 Separation of bacteria from mineral oil with different polymers

To a rolling oil (Roll oil 450, Nynäs) bacteria cells (Pseudomonas spp) with a size of about 2 µm were added. The concentration of bacteria was measured by means of a HACH turbidity meter. 8 g bacteria contaminated oil and 0.2 g of the polymers mentioned above were added to a 10 ml test tube of glass. A test tube containing 8 g bacteria contaminated oil without any added polymer was used as reference.

The contents of the test tubes were well mixed and centrifuged at 2 000 rpm during 2 minutes, after which 4 ml of the upper oil phase was transferred to clean trays of glass for measurement of the turbidity. The trials were carried out at room temperature.

Results from the separation of bacteria cells from a mineral oil (rolling oil) with and without polymer dosing is presented in Table 2. Without any added polymers a separation efficiency of 30 % was obtained after centrifugation at 2 000 rpm during 2 minutes. Corresponding results with the different polymers varied between 80 and 90 %. Addition of the positively charged hydroxyethyl-tallow oil-imidazoline gave also in this trial an increased bacteria separation (86-95 %) also for Breox 380EP.

Table 2

Polymer	Bacteria reduction
Propylene glycol (MB Sveda Kemi)	88.4
Propylene glycol + Berol 594	94.2
Polypropylene glycol 425 (MB Sveda Kemi)	80
Polypropylene glycol 425 + Berol 594	86
Breox 50A140 (BP, Chemicals)	88.4
Breox 50A140 + Berol 594	93.2
Breox 50A1000 (BP, Chemicals)	89.7
Breox 50A1000 + Berol 594	93.1
Breox 380EP (BP, Chemicals)	88.8
Breox 380EP + Berol 594	90.9
None	21.5

<u>Trial 3 Step-by-step purification of particle contaminated cutting oil by means of polymers</u>

To a particle contaminated straight cutting oil (Volvo, Skövde) 2.5 % (w/w) of the following polymer mixtures were added:
* 12 % Dapral 210 (Akzo) dissolved in propylene glycol
* 12 % Dapral 210 (Akzo) dissolved in propylene glycol + 3 % Berol 594

The addition was carried through in 10 ml test tubes of glass. After addition the contents of the tubes were mixed thoroughly after which they were centrifuged at 2 000 rpm during 2 minutes. As a control a sample of particle contaminated cutting oil without any addition of polymer was centrifuged. After removal of the particle containing polymer rich bottom phase the particle content in the upper oil phase was determined by means of a HACH turbidimeter. The extraction procedure was repeated twice. The turbidity was determined after each of the three centrifugations. The trials were carried out at room temperature.

Purification of a particle-contaminated cutting oil with and without addition of polymer is presented in figure 1. The addition of polymers was carried out step-by-step in order to simulate the continuous polymer addition which may be used when using centrifugal separators. Three successive centrifugations of the cutting oil at 2 000 rpm reduced the content of particles by 1 %. Addition of the polymer Dapral 210 dissolved in propylene glycol gave in the first extraction step 93 % separation efficiency and after two and three extractions the separation efficiency was 98 and 99 %, respectively. By including the positively charged polymer hydroxyethyl-tallow oil-imidazoline an increased separation efficiency was obtained which after three extractions was >99 %.

<u>Trial 4</u> <u>Purification of oil with polymer addition in combination with a centrifugal separator on a large scale</u>

Polymer particles with a median diameter of 4.3 µm (Expancel 051 DC) were added to 200 litres of oil (Nynäs). The oil was heated by means of an immersion heater to 55°C. The particle-contaminated oil was fed by way of a pump to a two-ways centrifugal separator (MMPX 304, Tetra-Laval AB, Tumba). The flow through the separator was 500 litres/hour. By way of a tube pump connected to the inlet to the separator poly-propylene glycol (Mw 425) was added. The flow of collection polymer was 3 litres/hour. The concentration of particles in the effluent from the separator was measured with and without addition of polymers by means of a HACH turbidity meter.

Industrial separators are commonly used to purify mineral oils from particulate contaminants and water on a large scale. Great application areas are purification of fuel and of lubricating systems on board of ships and within the industry. Purification from particles only by means of centrifugal separator does not give a satisfactory result in many cases which means that one has been forced to combine this technique with other purification methods, e.g. filtration. Addition of small amounts of polymer to particle-contaminated mineral oil in combination with separation of the polymer phase with an industrial separator results in a dramatical increase in the efficiency of separation (Table 3).

TABLE 3

Particle concentration (NTU) in the effluent with and without an addition of polymers. The concentration in the tank at start was 1960 NTU.

Time (min.)	Without polymer	With polymer
5	1725	4.9
10	1465	2.3
15	1399	2.0
20	1352	1.4

Only separation at a high g-force brings as may be seen from the table a low separation efficiency (9 -31 %) counted on the original concentraton in the oil. Addition of 0.6 % polypropylene glycol to the oil prior to the separator increased the separation efficiency dramatically as regards the particles (99.8 - 99.9 %). The advantage of this technique of purifying oil compared to the filter technique is that the problem with clogged filter pores is avoided. Since the distribution coefficient for the particles to the bottom phase polymer is extreme it is also possible to recirculate the bottom phase polymer, which means that very large volumes of oil may be purified with small volumes of polymer.

Trial 5 Purification of hydraulic oil contaminated by particles by means of polymer addition in combination with centrifugal separation on a large scale

A hydraulic oil (Load Way EP 220, Stat Oil) heavily contaminated with coke particles was heated to 80°C. The hydraulic oil was fed by way of a pump to a centrifugal separator (MMPX 304, Tetra Laval AB, Tumba). The flow through the separator was 500 l/h. A mixture of polypropylene glycol (MW 425) and Berol 594

(mixing ratio 5:1) was added to the feed inlet to the separator by way of a tube pump. The flow of collection polymer was 500 l/h. The concentration of particles in the effluent from the separator was measured by means of a HACH turbidity meter with and without addition of polymers.

The results from the trials with and without addition of polymer/imidazoline is given in table 4. As may be seen in the table centrifugal separation only gives a reduction of particles in the oil corresponding to about 73-78 %. This reduction is probably a decrease of the amount of larger particles but a gradual increase in the number of very small particles 0,1 - 3 µm in the hydraulic oil. Addition of polymer/Berol 594 gives an essentially increased separation efficiency corresponding to 99,3 - 99,6 %. With this addition a reduction of all present particle sizes takes place, i.e. also of particles of submicron size.

TABLE 4

Concentration of particles (NTU) in effeluent with and without addition of polymers. The initial concentration in the tank was 1230 NTU.

Time (min.)	Without polymer	With polymer
5	335	6.8
10	311	5.2
15	268	8.8
20	306	5.6

Trial 6 Separation of water in oil by means of polymer system

0.5 g H_2O was added to a test tube containing 19.5 g oil. The content of the tube was mixed well on a shaking device for test tubes and in a ultrasonic bath until the water was well emulsified into the oil phase. The water containing oil was divided into four test tubes after which the turbidity was determined. To tube A 2.5 % polypropylene glycol was added, to tube B 2.5 % polypropylene glycol containing 10 % Berol 594 and to the tube C 2.5 % polypropyleneglycol containing 20 % Dapral 210. The tubes were centrifuged together with a reference sample at 2 000 rpm during 6 minutes. After the centrifugation the turbidity in the oil phase was measured in all the tubes.

Separation of water in oil is a usual application for industrial separators. The technique may be improved considerably by additon of polymer/polymer mixtures (Table 5).

TABLE 5

Purification of oil as regards water by means of addition of polymers. The water content is given as turbidity in the oil (NTU).

	No polymer	Polypropylene glycol	Polypropylene glycol + Berol 594	Polypropylene glycol+ Dapral 210
0-sample	2110	2050	2089	2167
After centrifug.	784	11	14	14
Purifica-tion eff. (%)	63	99.5	99.3	99.4

As may be seen in the table there is a purification efficiency obtained around 60 % by using only centrifugation at 2 000 rpm during 2 minutes of oil containing very small water drops. By addition of polypropylene glycol, polypropylene glycol with addition of Berol 594 or polypropylene glycol with addition of Dapral 210 in all cases a separation efficiency >95 % is obtained. The polymers which are used in this trial are all water soluble but not soluble in oil.

Trial 7 Regeneration of polymer phase by means of citric acid/citrate buffer

To test tubes containing 10 g polypropylene glycol, (Mw 450) contaminated Expancel particles and bacteria cells there was added a 20 % citric acid/citrate buffer to a final concentration of 3.3 %. The relation between citric acid and citrate was 1:1. The test tubes were well mixed and centrifuged at 2 000 rpm during 2

minutes. The upper top phase rich in polypropylene glycol was analyzed by means of turbidity measurement.

Particle containing poylmer phase from oil purification may be regenerated by means of polymer two-phase-systems, where the polymer phase is the top phase and a water solution of citrate/citric acid, sodium or potassium phosphate buffer constitutes the bottom phase. In fig 2 there is shown a phase diagram for polypropylene glycol 425 and phosphate buffer. By dosing low concentrations of phosphate buffer in combination with a high polymer concentration there is formed, as may be seen in the figure, a system with a very small amount of bottom phase in which particulate contaminants from the polymer phase are concentrated.

Regeneration of collection polymer (polypropylene glycol 425) containing Expancel particles and bacteria cells (Pseudomonas spp) by means of a water containing polymer two-phase system consisting of citric acid/citrate buffer as a bottom phase polymer is shown in Table 6.

TABLE 6

Regeneration of collection polymer phase by means of a water containing polymer two-phase system. The particles consist of Expancel particles and bacteria cells. The particle concentration in the polymer phase is given in NTU.

	Expancel particles	Bacteria cells
Particle content polymer phase prior to separation	4790	2620
Particle content polymer phase after separation	420	170
Regenerative eff.	91	94

As may be seen in the table there a good separation efficiency 91-94 % is obtained of the polymer phase after only one separation with citric acid/citrate buffer. At the addition of buffer solution to the polymer a certain part of water will be found in the polymer phase when the two phase system is formed. This water amount is very small <6 % and will not effect the separation efficiency when the polymers are used for purification of mineral oils.

An arrangement for purification of oil will be described with reference to fig 3.

In this figure there is shown a central collection tank for contaminated oil 1. From this tank the oil is led towards a centrifugal separator 2 by way of a pipe 3. In this pipe there is a pump 4 where the oil is mixed with polymers according to the invention. The oil and the polymers are separated in the centrifugal separator and the purified oil is returned to the tank 1 by way of pipe 5. The polymers and the particles are led to a second purification step where the polymers are regenerated by way of a pipe 6. In this step there is a

tank 7 for a citric acid/citrate buffer. The mixture of polymer and particles are mixed with the citric acid/citrate buffer in a further pump 8 and led to a second centrifugal separator 9. The purified polymer phase is returned to the polymer tank by way of pipe 10, while the contaminants are removed by way of pipe 11.

Claims

1. Method for purification of oil which is contaminated by particles of random density and/or water, c h a r a c t e r i z e d i n that a collection polymer or polymer mixture, which polymer or polymer mixture is insoluble in oil and liquid at room temperature and has a density which is higher than the oil, is added to and mixed with the contaminated oil, that the collection polymer and the oil are separated by gravity with or without centrifugation such that the oil forms a top phase and the collection polymer or polymer mixture and the main part of the contaminants form a bottom phase; and that the bottom phase with the collection polymers and the contaminants is removed.

2. Method according to claim 1, c h a r a c t e r i z e d i n that a charged control polymer is added together with the polymers, which control polymer is reacting with contaminants in the oil in such a way that the amount of contaminants in the bottom phase is increased.

3. Method according to claim 1 or 2, c h a r a c t e r i z e d i n that the oil is subjected to repeated purification.

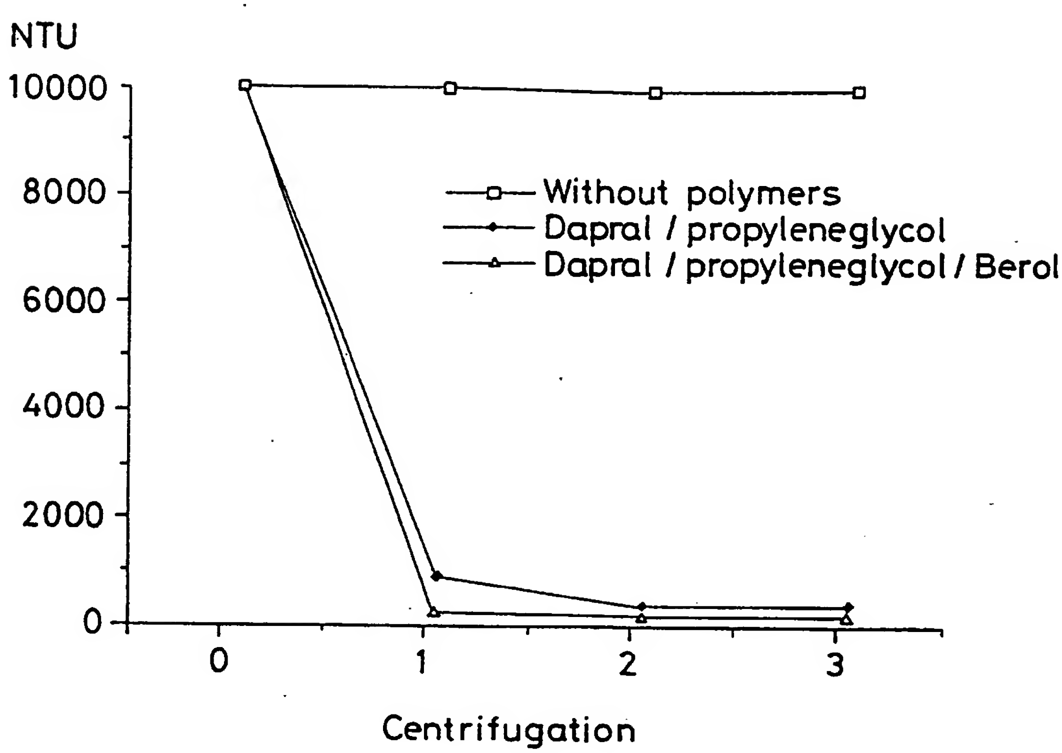
4. Method according to any of the claims 1-5, c h a r a c t e r i z e d i n that the collection polymer or polymer mixture is recovered by regeneration by means of a polymer two-phase system.

5. Method according to any of the claims 1-4, c h a -

r a c t e r i z e d i n that a complex forming agent is added together with the collection polymer or polymer mixture.

6. Use of a collection polymer or polymer mixture insoluble in oil for purification of a contaminated oil by gravity with or without centrifugation.

7. Polymer mixture comprising a collection polymer insoluble in oil, a charged control polymer and a complex forming agent.



NTU
10000
8000
6000
4000
2000
0
0
1
2
3
Centrifugation
Without polymers
Dapral / propyleneglycol
Dapral / propyleneglycol / Berol

Fig.1

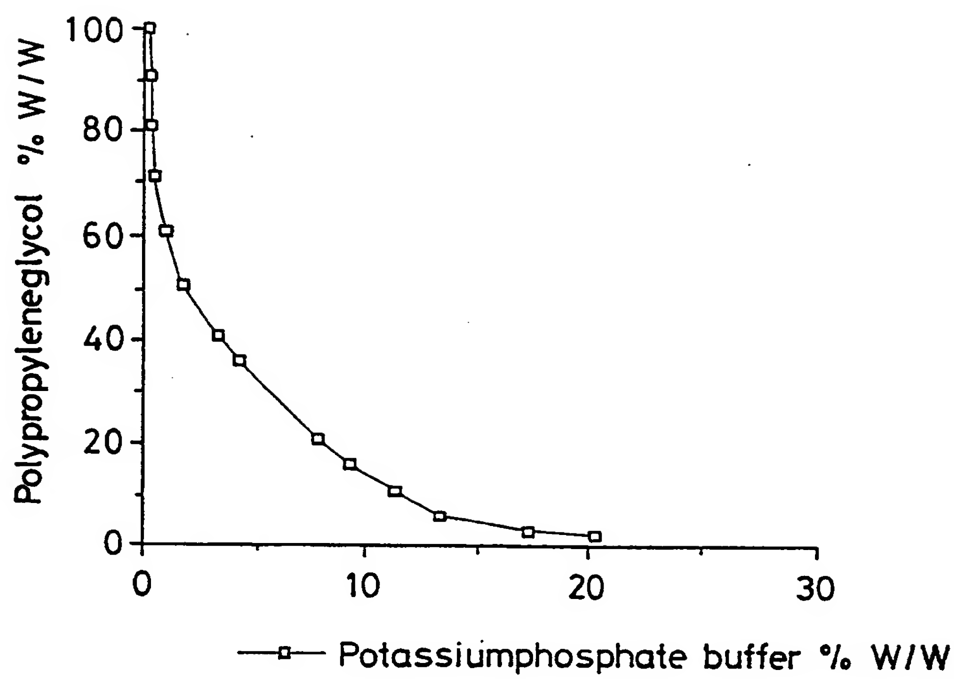

Polypropyleneglycol % W/W
100
80
60
40
20
0
0
10
20
30
Potassiumphosphate buffer % W/W

Fig.2

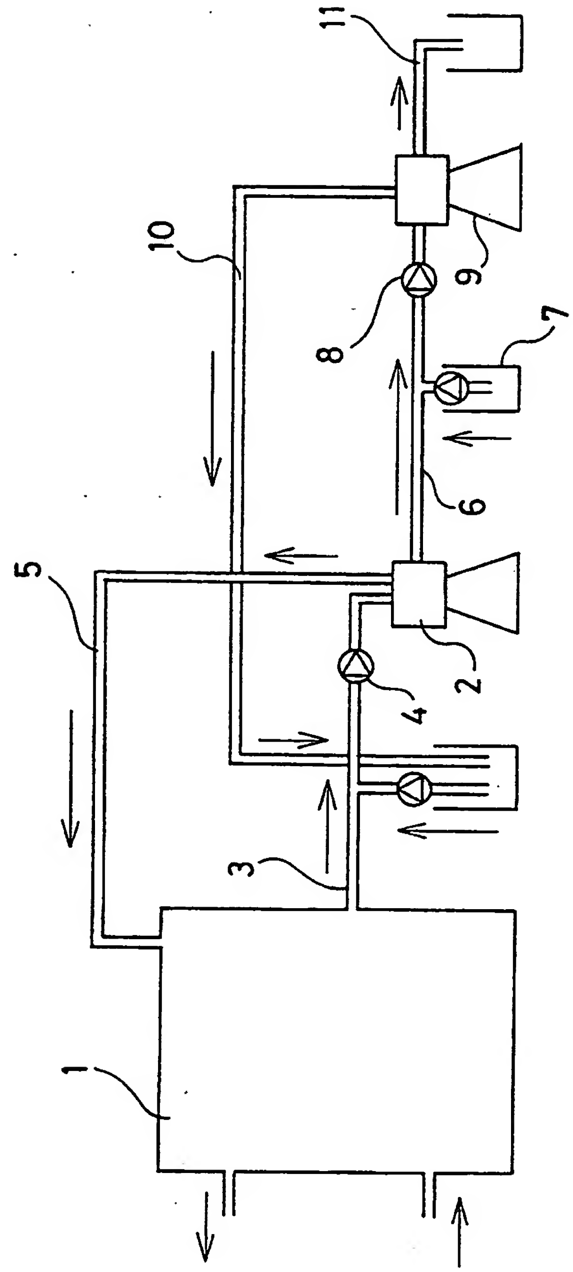


Fig.3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 94/01136

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C10M 175/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C10M, B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5141628 (ERICH-KLAUS MARTIN ET AL), 25 August 1992 (25.08.92), column 7, line 44 - line 48	1,3,5,6
Y		2,4,7
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Y	WO, A1, 9005768 (PEGASUS SEPARATION AB), 31 May 1990 (31.05.90), page 9, line 6 - line 19	2,4,7
	--	
X	EP, A1, 0493693 (BAYER AG), 8 July 1992 (08.07.92), see the abstract, page 5, line 23-34	1,3,5,6
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
28 February 1995	06 -03- 1995
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INTERNATIONAL SEARCH REPORT
Information on patent family members

09/02/95

International application No.
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